Atmospheric Pollutants and Trace Gases

Crusting of Stored Dairy Slurry to Abate Ammonia Emissions: Pilot-Scale Studies

Tom H. Misselbrook,* Siobhan K. E. Brookman, Ken A. Smith, Trevor Cumby,
Adrian G. Williams, and Dan F. McCrory

ABSTRACT

Storage of cattle slurry is a significant source of ammonia (NH_3) emissions. Emissions can be reduced by covering slurry stores, but this can incur significant costs, as well as practical and technical difficulties. In this pilot-scale study, slurry was stored in small tanks (500 L) and the effectiveness of natural crust development for reducing NH_3 emissions was assessed in a series of experiments. Also, factors important in crust development were investigated. Measurements were made of crust thickness and specially adapted tank lids were used to measure NH_3 emissions. Slurry dry matter (DM) content was the most important factor influencing crust formation, with no crust formation on slurries with a DM content of <1%. Generally, crusts began to form within the first 10 to 20 d of storage, at which time NH_3 emission rates would decrease. The formation of a natural crust reduced NH_3 emissions by approximately 50%. The type of bedding used in the free stall barn did not influence crust formation, nor did ambient temperature or air-flow rate across the slurry surface. There was a large difference in crust formation between slurries from cattle fed a corn (*Zea mays* L.) silage–based diet and those fed a grass silage–based diet, although dietary differences were confounded with bedding differences. The inclusion of a corn starch and glucose additive promoted crust formation and reduced NH_3 emission. The maintenance of a manageable crust on cattle slurry stores is recommended as a cost-effective means of abating NH_3 emissions from this phase of slurry management.

Agriculture is the major source of anthropogenic ammonia (NH_3) emissions to the atmosphere (Davidson and Mosier, 2004). Atmospheric transport and subsequent deposition of emitted NH_3 can damage fragile ecosystems and this has led to international pressures to reduce such emissions (United Nations Economic Commission for Europe, 1999). Emissions from livestock housing and manure applications to land represent the major emission sources within UK agriculture, but emissions from manure storage are also significant, representing approximately 10% of total NH_3 emissions from UK agriculture (Pain et al., 1998; Misselbrook et al., 2000). Storage is also a phase of manure management where cost-effective abatement of emissions might be achieved.

Substantial reductions in emissions of NH_3 from slurry storage can be achieved by the fitting of rigid covers or the use of a variety of materials (straw, clay granules, oil, peat) as a floating cover, all of which have been shown to give reductions in excess of 80% (de Bode, 1991; Sommer et al., 1993; Sommer, 1997; Hornig et al., 1999; Scotford and Williams, 2001; Portejoie et al., 2003; Bicudo et al., 2004). However, rigid covers are expensive to fit to stores and there can be problems maintaining floating covers. The development of a natural crust on the slurry surface has the potential to be equally effective as other covers at reducing emissions. De Bode (1991) found that NH_3 losses were reduced by 0 to 37% when a natural crust was formed and by 63 to 79% if the crust was improved by straw addition. Sommer et al. (1993) also reported 80% reduction in emissions with the presence of a natural crust.

Natural crust development represents an effective and inexpensive alternative to artificial store covers, but little is known about the process of crust development or which properties of a crust are important in reducing NH_3 emissions. It is hypothesized that crust development occurs as a result of solids in suspension in the stored slurry being carried to the surface by bubbles of gas (carbon dioxide, methane) generated by microbial degradation of the organic matter. Evaporation at the surface will promote drying and binding of the particles at the slurry surface, forming a crust. The concentration and nature of the solids present in the slurry, which in turn may be influenced by the cattle diet and bedding material used, are therefore likely to be important in determining crust formation together with the environmental factors (temperature, wind speed, rainfall) influencing surface drying. The objectives of this study, therefore, were to (i) investigate the factors influencing crust development on cattle slurry stores, (ii) confirm that effective emission reductions are achievable with

T.H. Misselbrook and S.K.E. Brookman, Institute of Grassland and Environmental Research, North Wyke, Okehampton, Devon EX20 2SB, UK. K.A. Smith, ADAS, Woodthorne, Wergs Road, Wolverhampton WV6 8TQ, UK. T. Cumby and A.G. Williams, Silsoe Research Institute, Wrest Park, Silsoe, Bedfordshire MK45 4HS, UK. D.F. McCrory, USDA-ARS, Dairy Forage Research Center, University of Wisconsin, 1925 Linden Drive West, Madison, WI 53706. Received 3 June 2004. *Corresponding author (tom.misselbrook@bbsrc.ac.uk).

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677 S. Segoe Rd., Madison, WI 53711 USA

Abbreviations: DM, dry matter; TAN, total ammoniacal nitrogen; TAN_i, initial total ammoniacal nitrogen.

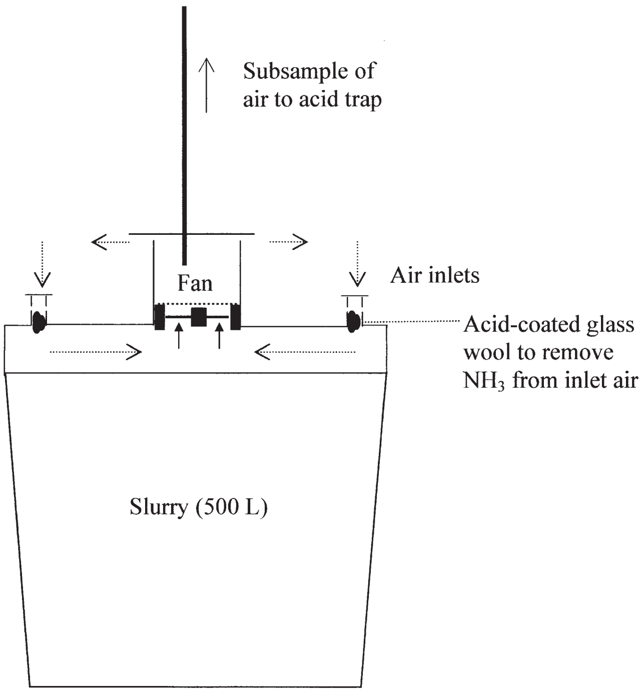

Fig. 1. Schematic diagram of pilot-scale slurry store with adapted cover for measurement of ammonia emissions.

a natural crust, and (iii) assess which crust properties influence the emission reductions that are achieved.

MATERIALS AND METHODS

Pilot-Scale Slurry Stores

The study was conducted at the North Wyke Research Station in Devon, UK. Locally sourced dairy cattle slurry was stored in plastic water tanks (Merlin AX100; T & D Plastech, Bradford, UK) for periods of between 45 and 110 d. This represents the lower end of the typical 90- to 180-d storage capacity of UK dairy and beef farms (Smith et al., 2001), but was regarded as sufficient duration to study the process of crust formation. The tanks had a 680-L total capacity, 0.75-m height, 0.93-m base diameter, and 1.06-m top diameter. When filled with 500 L of slurry there was a freeboard of 0.12 m between the slurry surface and top of the tank. For the initial experiments (1, 2, and 6), tanks were positioned outside without lids, but with raised wooden covers to exclude rainfall while allowing natural airflow over the slurry surface. At intervals, NH_3 emission measurements were made by placing specially adapted lids (see Fig. 1) on each tank. For later experiments (3–5), the tanks were kept indoors for the storage period, with the specially adapted lids in place for the entire storage period.

Crusting Observations and Ammonia Emission Measurements

Observations of crust formation were made on a weekly basis. Records were made of the proportion of the surface covered by crust (visual assessment), whether the crust surface was wet or dry, and the crust thickness. Crust thickness was measured by inserting a graduated (0.01-m increments) plastic tube through the crust and inflating a small rubber sac below the crust with 0.1 L of air. The device was then allowed to float up until the air-filled sac rested beneath the crust and the reading of crust thickness could then be made from the graduated tube at the upper surface of the crust.

The circular lids supplied with the storage tanks were modified to form NH_3 emission sampling lids (Fig. 1). A centrally located fan (0.16-m diameter) drew air across the slurry surface through six inlet holes (0.03-m diameter) cut at regular intervals around the perimeter of the lid. Acid-coated glass wool (soaked for 1 h in 3% tartaric acid solution in methanol) was placed across the inlet holes to remove any NH_3 from the inlet air. The glass wool was replaced at the beginning of each experiment. Ammonia concentration of the outlet air was determined by drawing a subsample of the air through an absorption flask containing dilute (0.01 M) orthophosphoric acid. Concentration of NH_4^+–N in the absorption flask (C_l, g N L^{-1}) was determined using automated colorimetry (Searle, 1984), from which the concentration of NH_3 in the outlet air (C_a, g N m^{-3}) was determined according to:

$$C_a = C_l V_l / V_a \quad [1]$$

where V_l is the volume of acid (L) and V_a the volume of sampled air (m^3), measured using gas meters. The emission rate from the tank could then be calculated as the product of the concentration in the outflow air and the air flow rate through the central duct of the lid, determined using a handheld anemometer (Model LCA6000, calibrated annually; Airflow Instrumentation, High Wycombe, UK). Emission rates were measured over a 2-h period, at least twice during the first week of storage and, thereafter, at weekly intervals. Unless included as a variable, fans were set to draw air at 2 m s^{-1} through the central duct, equating to a wind speed across the slurry surface of approximately 0.2 m s^{-1} and approximately 23 headspace changes per minute.

Treatments

Six experiments were performed to assess a range of factors influencing crust formation, including cattle bedding type, cattle diet, slurry dry matter (DM) content, air flow above the slurry surface, rainfall, and use of a starch and glucose additive (Table 1). With the exception of Experiment 5, all slurries were collected from the dairy herd at the Institute of Grassland and Environmental Research (IGER), North Wyke. The cows were housed in a free stall barn with sawdust bedding (except for Experiment 1) and fed a mixed grass and corn silage diet. Slurry samples were taken at the start of each experiment

Table 1. Details of the pilot-scale slurry storage experiments.

Experiment	Factors	Storage dates	Location	Replicates
1	bedding type	February–May 2000	outdoor	4
2	slurry DM† content	July–October 2000	outdoor	4
3	slurry DM content	July–October 2002	indoor	3
4	air flow rate	April–June 2002	indoor	4
5	diet, rainfall	January–March 2003	indoor	3
6	additive	July–October 2000	outdoor	4

† Dry matter.

Table 2. Analyses of the slurries at the beginning of each experiment.†

Treatment‡	Dry matter	pH	Total ammoniacal N	Total N	Slurry temperature Mean	Range
	%		g L^{-1}		°C	
Experiment 1						
No bedding	7.0 (0.33)	6.8 (0.01)	0.8 (0.01)	2.5 (0.06)	6.0	2.7–17.4
Sawdust	8.5 (0.64)	6.8 (0.03)	0.9 (0.00)	2.5 (0.05)		
Shredded paper	5.9 (0.56)	6.8 (0.03)	0.9 (0.00)	2.4 (0.10)		
Chopped straw	6.0 (0.95)	6.8 (0.03)	1.0 (0.01)	2.2 (0.09)		
Experiment 2						
DM1	0.9 (0.03)	6.9 (0.04)	0.5 (0.00)	0.8 (0.01)	13.2	9.3–19.4
DM2	5.0 (0.07)	6.8 (0.01)	0.9 (0.01)	2.0 (0.01)		
DM3	6.6 (0.19)	6.7 (0.01)	0.9 (0.01)	2.3 (0.05)		
Experiment 3						
DM1	1.2	6.7	0.6	ND§	16.1	10.9–20.2
DM2	2.2	6.8	0.8	ND		
DM3	4.0	6.8	0.9	ND		
DM4	5.9	7.2	0.8	ND		
Experiment 4						
FS1						
FS2	7.0 (0.40)	7.0 (0.04)	0.8 (0.01)	ND	15.1	11.5–17.6
FS3						
Experiment 5						
GDC	7.8 (0.03)	ND	0.9 (0.08)	ND	13.5	10.6–15.7
CDC						
CWC	7.8 (0.05)	ND	1.3 (0.04)	ND		
CDWC						
Experiment 6						
No additive						
High-starch additive	5.1 (0.10)	6.9 (0.04)	0.9 (0.01)	2.0 (0.02)	13.2	9.1–24.0
Low-starch additive						

† Values in parentheses are standard errors of the mean.
‡ DM, dry matter; FS, fan speed; GDC, grass silage, dry crust; CDC, corn silage, dry crust; CWC, corn silage, wet crust; CDWC, corn silage, dry then rewetted crust.
§ Not determined.

for chemical analyses (DM content, pH, total N, and total ammoniacal nitrogen [TAN] content).

In Experiment 1, slurry was collected from dairy cattle kept on four bedding types: sawdust, chopped straw, shredded paper, or no bedding. Ten cows were bedded in a free stall barn on each of these bedding types and slurry was collected each day from the manure passage over a 2-wk period. Water was added to each slurry in an attempt to standardize DM content at 6%. In Experiments 2 and 3, different slurry DM contents were achieved through a combination of settlement and dilution, with three DM contents in Experiment 2 (DM1–DM3; Table 2) and four in Experiment 3 (DM1–DM4; Table 2). In Experiment 4, a speed controller was incorporated in the fans in the central duct of the sampling lid, such that different flow rates could be achieved (1.4, 1.7, and 2.1 m s^{-1} for Treatments FS1, FS2, and FS3, respectively, equating to 0.14, 0.17, and 0.21 m s^{-1} across the slurry surface and 15, 19, and 23 headspace changes per minute). In Experiment 5, slurries were collected from two local commercial dairy cattle herds, one fed a grass silage–based diet and the other corn silage–based. Three tanks were filled with the slurry from the cattle on the grass silage–based diet. These were left to crust with no further intervention (grass, dry crust [GDC]). Nine tanks were filled with slurry from the cattle on the corn silage–based diet. Three of these were left, as with the grass silage treatment (corn, dry crust [CDC]). Three had simulated rainfall applied twice per week, with 5 L of water via a watering can with a rose (corn, wet crust [CWC]). This simulated rainfall of approximately 6 mm on each occasion. The remaining three were left for 4 wk and then had simulated rainfall twice per week for the remaining 2 wk (corn, dry then rewetted crust [CDWC]). Diet and bedding were confounded in this experiment, with the cattle fed the grass silage–based diet bedded on long straw and those fed the corn silage–based diet bedded on chopped straw.

Experiment 6 was designed to assess the effect of a corn starch and glucose additive on NH_3 emissions, which were measured periodically as described above. No crust thickness measurements were made in this experiment, although photographic evidence of crusting was taken after 27 d. Three treatments were included: slurry without any additive, slurry with a high-starch additive (80% starch, 20% glucose), and slurry with a low-starch additive (50% starch, 50% glucose). The additive was applied at an overall dosage of 0.2% (w/v) evenly over the slurry surface immediately after slurry was placed in the stores. These rates and method of inclusion were chosen based on the results of laboratory-scale studies with this additive (McCrory, 2003).

For all experiments, temperature was continuously logged (hourly averages) from one replicate of each treatment via thermistors at a 15-cm depth.

Slurry Analyses

The slurry samples taken at the beginning of each storage period were analyzed for DM, total N (not all samples), TAN, and pH. Dry matter was determined by drying a 0.1-L subsample of slurry to a constant weight at 100°C. Total N concentration was analyzed using a macro-Kjeldahl technique (Anonymous, 1986). Slurry TAN content was determined by extracting with 2 *M* potassium chloride followed by automated colorimetry (Searle, 1984).

Statistical Analyses

There were either three or four replicates of each treatment in the experiments (Table 1). To account for differences in slurry TAN contents between treatments and between experiments, emission rates were normalized:

$$\text{NER} = (\text{ER}/\text{TAN}_i) \times 100 \quad [2]$$

where ER is the measured emission rate (g N m^{-2} d^{-1}), NER is the normalized emission rate (% TAN_i m^{-2} d^{-1}), and TAN_i is the initial TAN content (g N).

The analysis of variance procedure of GENSTAT (Lawes Agricultural Trust, 1993) was used to determine significant differences in NH_3 emission rates, normalized emission rates, cumulative emission, and crust thickness between treatments within each experiment.

RESULTS

Slurry Analyses

Analyses of the slurries at the beginning of each experiment (after DM adjustment for Experiment 1) are given in Table 2, together with the mean and range in slurry temperature over the storage period.

Experiment 1: Effect of Bedding Material

There were some differences in the DM contents of the slurries from the different bedding types ($p = 0.05$), although all slurries were of a comparatively high DM content (for UK dairy cattle slurry). Slurry pH values were constant across all treatments and total N contents were similar, but there were small differences in TAN contents.

Crusts developed on all treatments, first as a “skin” and then as a measurable crust by Day 20 (Fig. 2). There were no significant differences ($p > 0.05$) in crust thickness until the final measurement at 110 d, when the no bedding treatment had a significantly thinner crust than the other treatments. There were no significant treatment differences ($p > 0.05$) in emission rates or normalized emission rates and no significant trends in emission rates with time, although no emission measurements were made after 80 d. The mean emission rate over the measurement period for all treatments was 2.3 g N m^{-2} d^{-1}, a mean normalized emission rate of 0.5% TAN_i m^{-2} d^{-1}.

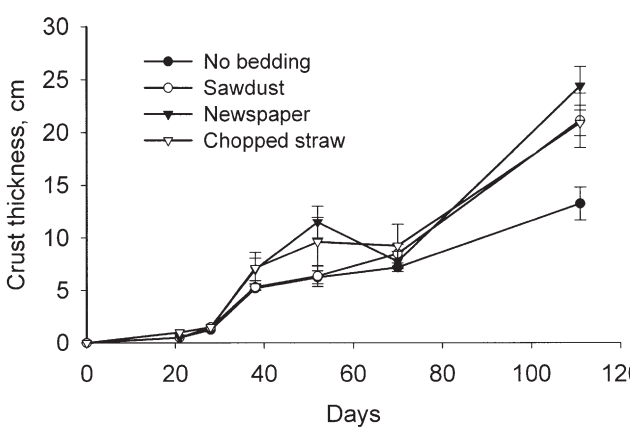

Fig. 2. Influence of bedding type (Experiment 1) on crust formation. Error bars indicate ±1 standard error of the mean (n = 4).

Experiments 2 and 3: Effect of Slurry Dry Matter Content

In Experiment 2, the range of slurry DM contents achieved was skewed, with one very dilute slurry and two thicker slurries. The dilute slurry had a lower NH_4^+–N and total N content, whereas those of the thicker slurries were similar to each other. Slurry pH was similar for all three treatments. Crust thickness was only measured on two occasions (Fig. 3a). A thick crust had developed on the two higher DM slurries by Day 43, with crust thickness being greater on the highest DM slurry ($p <$ 0.05). The crust thickness increased on the DM2 treatment between Days 43 and 94, whereas that of DM3 remained the same. No crust formation was noted on the dilute slurry (DM1). It was noted that the crust surface on DM2 and DM3 remained wet throughout the first 60 d of the storage period.

Emission rates were greater than in Experiment 1 (Fig. 3b), with a mean overall treatments of 8.6 g N m^{-2} d^{-1}. For most of the storage period, there were no significant differences ($p > 0.05$) in emission rates between treatments. However, toward the end of storage, the emission rates from the thicker slurries (DM2 and DM3) declined, whereas those from the more dilute

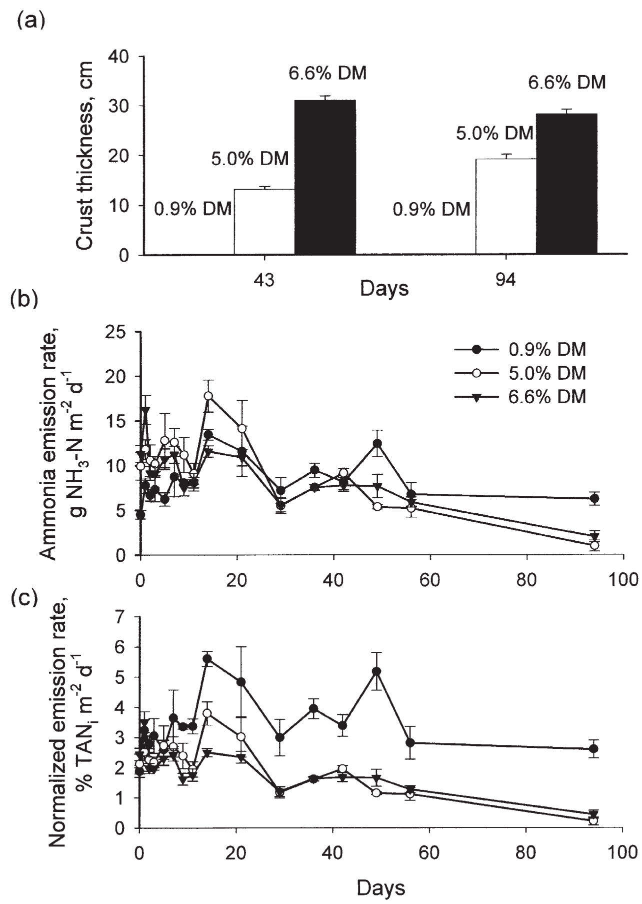

Fig. 3. Influence of slurry dry matter (DM) content (Experiment 2) on (a) crust thickness, (b) ammonia emission rate (g NH_3–N m^{-2} d^{-1}), and (c) normalized emission rate (% initial total ammoniacal nitrogen [TAN_i] m^{-2} d^{-1}). Error bars indicate ±1 standard error of the mean (n = 4).

slurry (DM1) remained closer to the initial rate. The decline in emission rates in DM2 and DM3 as crusts were forming is more obvious from the graph of the normalized emission rates (Fig. 3c), with significantly greater ($p < 0.05$) emission rates from DM1 (mean of 3.5% TAN_i m^{-2} d^{-1}) than from DM2 and DM3 (mean of 2.0% TAN_i m^{-2} d^{-1}) due to the lower initial TAN content of that treatment.

A more evenly distributed range in slurry DM contents was achieved in Experiment 3 than in Experiment 2. The TAN content of DM1 was lower than that of the other three treatments, whereas pH values were broadly similar. A "skin" began to form on the surfaces of all slurry treatments within the first week of storage. By Day 29 this had become a measurable crust on treatments DM3 and DM4 (Fig. 4a), but a thicker crust did not form on DM2 until Day 60, from which time onward it was not significantly different ($p > 0.05$) in thickness to DM3 and DM4. No measurable crust formed on DM1. Crusts on DM3 and DM4 were dry for most of the storage period, whereas the crust on DM2 remained wet until Day 70. The emission rates were inversely correlated with crust thickness ($r = -0.76$, -0.77, and -0.81 for DM2, DM3, and DM4, respectively), with rates from DM3 and DM4 declining throughout storage (Fig. 4b and 4c), whereas rates from DM2 remained higher initially, declining after Day 30. Rates from DM1 did not decline at all throughout the storage period. Mean emission rates were 5.9, 3.9, and 3.2 g N m^{-2} d^{-1} for DM1, DM2, and DM3–DM4, respectively, giving respective mean normalized emission rates of 2.0, 1.0, and 0.7% TAN_i m^{-2} d^{-1}.

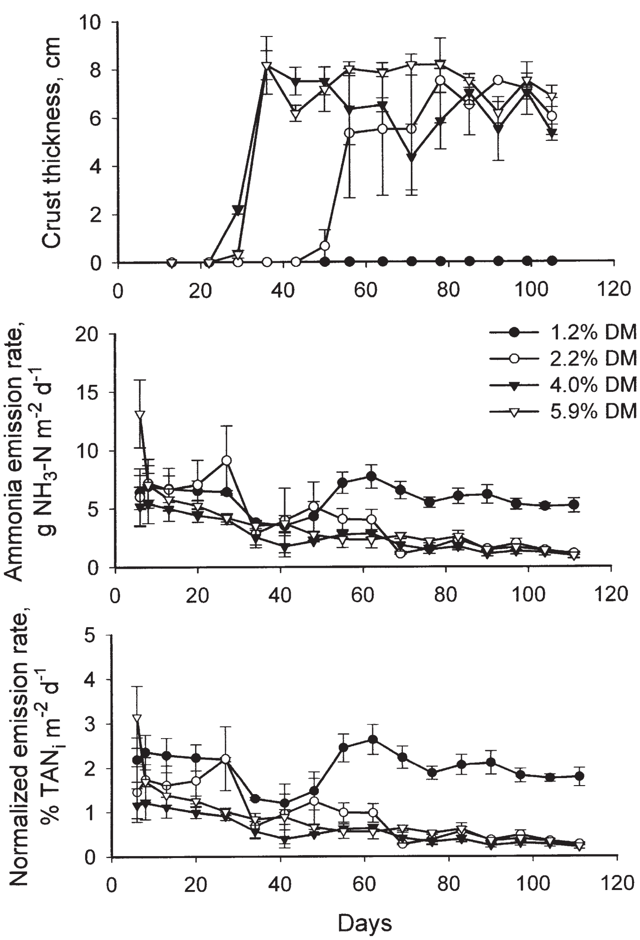

Fig. 4. Influence of slurry dry matter (DM) content (Experiment 3) on (a) crust formation, (b) ammonia emission rate (g NH_3–N m^{-2} d^{-1}), and (c) normalized emission rate (% initial total ammoniacal nitrogen [TAN_i] m^{-2} d^{-1}). Error bars indicate ±1 standard error of the mean ($n = 3$).

Experiment 4: Effect of Air Flow Rate

Only limited control of fan speed was possible with the fans used in these experiments and it would have been desirable to have had a larger range in air flow rates across the slurry surface, particularly to include some higher flow rates. There was no significant influence ($p > 0.05$) of air flow rate on crust development (Fig. 5a). Crusts formed rapidly on all treatments and remained dry throughout the storage period. Emission rates declined with crust formation (Fig. 5b) with rates increasing with air flow rate (although not always significantly). Mean emission rates were 1.7, 2.4, and 5.2 g N m^{-2} d^{-1} for FS1, FS2, and FS3, respectively. As the same slurry was used for all treatments, normalized emission rates showed the same pattern, with mean values of 0.4, 0.6, and 1.3% TAN_i m^{-2} d^{-1}, respectively.

Experiment 5: Effect of Diet and Rainfall

The slurry from the cattle on the corn silage– and grass silage–based diets had the same DM content, but differing TAN contents. There was a large difference ($p < 0.05$) in the rate and thickness of crust formation

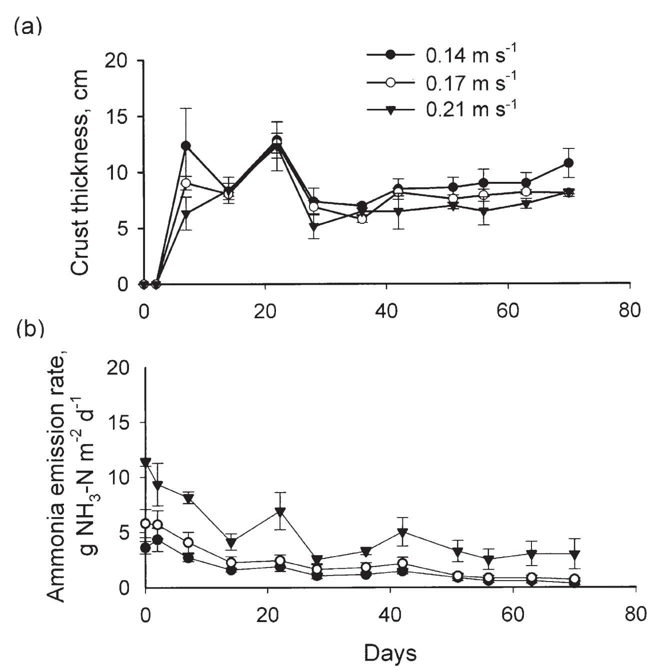

Fig. 5. Influence of air flow rate (Experiment 4) on (a) crust formation and (b) ammonia emission rate (g NH_3–N m^{-2} d^{-1}). Error bars indicate ±1 standard error of the mean ($n = 4$).

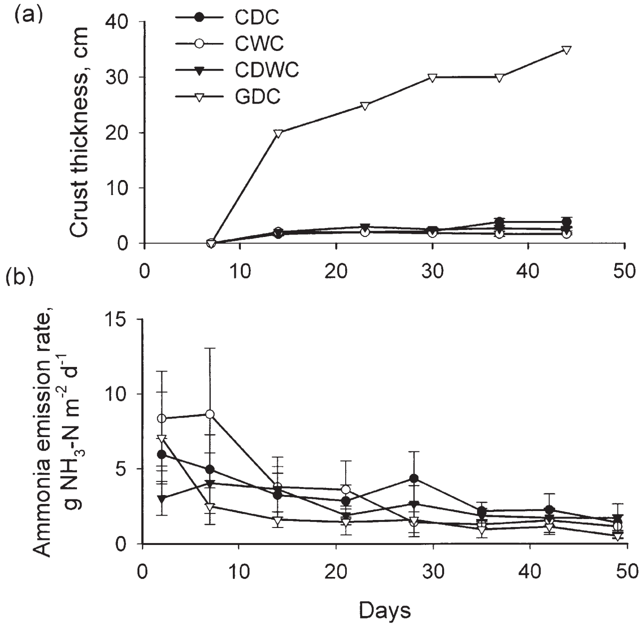

Fig. 6. Influence of cattle diet and rainfall (Experiment 5) on (a) crust formation and (b) ammonia emission rate (g NH_3–N m^{-2} d^{-1}). Error bars indicate ±1 standard error of the mean (n = 3). CDC, corn, dry crust; CWC, corn, wet crust; CDWC, corn, dry then rewetted crust; GDC, grass, dry crust.

on the slurries from the cattle on different diets (Fig. 6a). The slurry from the corn-fed cattle formed a thin but solid crust, which was dry apart from the simulated rainfall treatments. In fact, the crusts on the wetting treatments (CWC and CDWC) appeared to dry rapidly between the water applications. In contrast, the slurry from the grass-fed cattle rapidly formed a very thick, fibrous, but initially wet, crust, the depth of which was difficult to assess using the methodology described above. There were no significant differences ($p > 0.05$) in emission rates from the treatments (Fig. 6b), with emission rates declining over the storage period. Mean emission rate across all treatments was 3.0 g N m^{-2} d^{-1}, equivalent to a mean normalized emission rate of 0.5% TAN_i m^{-2} d^{-1}.

Experiment 6: Effect of Corn Starch and Glucose Additive

The corn starch and glucose additive was immediately effective in reducing emissions as compared with the control treatment (Fig. 7). The largest difference between treatments was over the first 11 d, where emissions from the low-starch treatment were significantly lower ($p > 0.05$) than those from the high-starch treatment. From Days 11 to 18, emission rates did not differ significantly between the additive treatments but both were significantly lower than the control ($p < 0.05$). After Day 18 there were no significant differences in emission rates between any treatments. Photographic evidence on Day 27 showed good crust development on the additive treatments, with obvious gas bubbling, and much poorer crust development on the control treatment (Fig. 8).

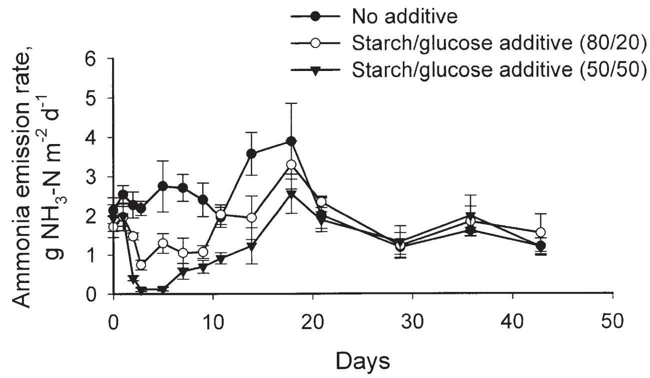

Fig. 7. Influence of a starch and glucose additive on ammonia emission rate (g NH_3–N m^{-2} d^{-1}). Error bars indicate ±1 standard error of the mean (n = 3).

DISCUSSION

Methodology

The tanks used in this pilot-scale study fall partway between laboratory chamber studies (e.g., Portejoie et al., 2003) and on-farm stores. In laboratory studies, the limited volumes (and depths) of slurry may lead to differences in the gas generation and emission processes as compared with an on-farm store, where measurements are subject to practical difficulties and are unsuitable for replicated factorial studies. In the earlier experiments, where lids were only placed on the tanks for the measurement periods, measured emission rates are likely to have differed from those between measurement periods; therefore, calculation of cumulative emissions from the tanks was not appropriate. For the latter experiments, where the lids were kept on throughout the storage period with a controlled air-flow rate, measured emission rates would be more representative of the emissions between measurement periods, although there may have been some variation due to diurnal temperature changes (the room was not at constant temperature). Air flow rates in all experiments were sufficient to give a minimum of 15 headspace changes per minute, above which it has been reported that differences in air flow rate will not influence NH_3 emission rate (e.g., Kissel et al., 1977). It was surprising, therefore, that in this study emission rates did increase with an increase in air-flow rate from 15 to 23 headspace changes per minute (Experiment 4).

The range in mean emission rates from slurries developing a crust in this study (1.7–8.6 g N m^{-2} d^{-1}) was similar to that from which the emission factor for cattle slurry storage (crusted) was derived for the UK NH_3 emissions inventory (0.5–5.7 g N m^{-2} d^{-1}), although the overall mean from this study of 4.4 g N m^{-2} d^{-1} was double the UK inventory emission factor of 2.2 g N m^{-2} d^{-1} (Misselbrook et al., 2000). In Experiments 2 and 3, the normalized emission rates for the noncrusted treatments (DM1 in each experiment) indicated that >100% of the TAN initially present in the slurry had been lost as NH_3. This may be partially accounted for by mineralization of the slurry organic N content (e.g., Whitehead and Raistrick, 1993; Beline et al., 1998), or may be an indication that the acid-coated glass wool on the air

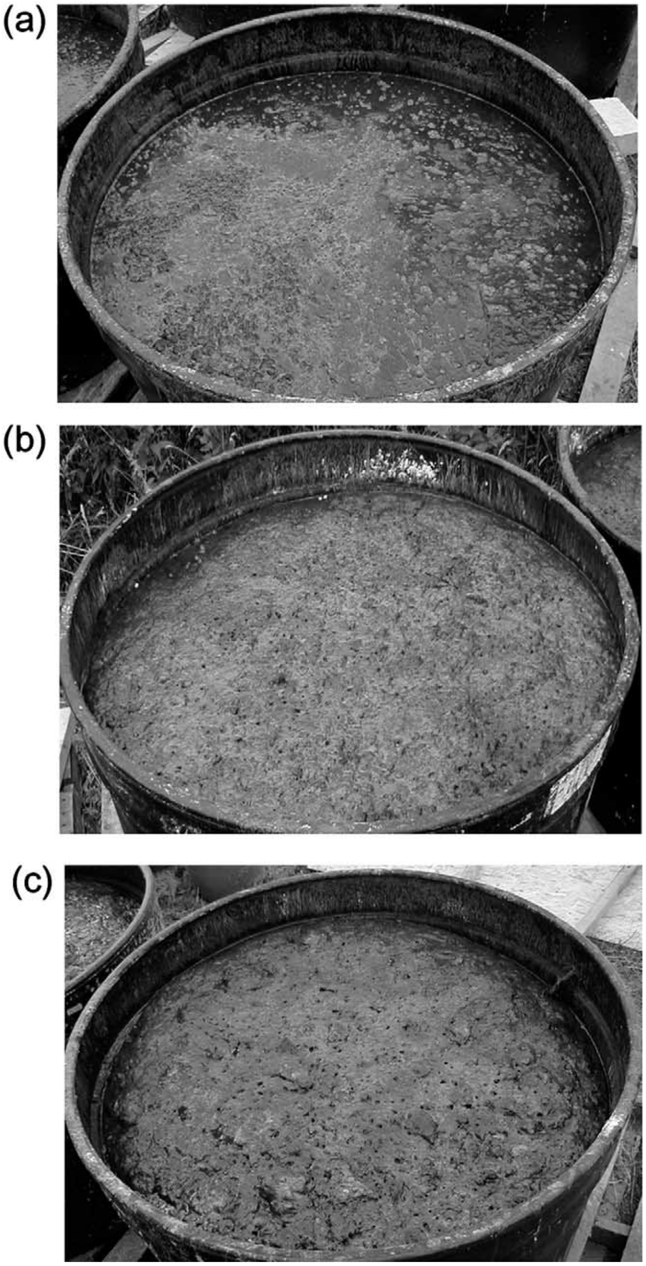

Fig. 8. Crust formation on (a) control, (b) high-starch, and (c) low-starch treatments, each after 27 d of storage. Tank dimensions: 0.75-m height, 1.0-m diameter, 500-L slurry volume. Differences can be seen between the watery thin "skin" in (a), the more significantly developed crust in (b), and the substantial "pie-crust" development in (c).

inlets of the lid was becoming saturated with NH_3. A refinement of the pilot-scale system would be to site all storage tanks in a controlled temperature environment with a clean inlet air supply and to duct all exhaust air away from the tanks. Such a system would provide a standard means of comparing storage treatments, as was recommended by McCrory and Hobbs (2001).

Crust thickness could be measured with the device used in this study to an accuracy of about ±1 cm once an integral crust of at least 1 cm had formed. The device was not suitable for measuring thinner crusts (described as a "skin" above). Development of techniques for measuring other properties of crusts that may influence emissions, such as wetness, strength, and porosity, might improve interpretation of results.

Crust Development and Ammonia Emission

In this study, where direct comparisons could be made in emissions from crusted and noncrusted slurry stores (Experiments 2 and 3), crusting reduced mean NH_3 emission rate by 51% over the duration of the storage period. Sommer et al. (1993), also using small-scale tanks (approximately 4 m^3 of slurry), reported that the formation of a natural crust reduced emission by 80%, compared with emissions from a stirred tank. The reduction in our study was not so large, but the control store was not stirred and formed a thin "skin" in most cases.

There was some evidence from this study of a decline in NH_3 emissions as crust thickness increased (Fig. 3–6), although this was not consistently observed (no effect in Experiment 1, the reasons for which are unclear, and no difference in emission rate between GDC and other treatments in Experiment 5 despite a large difference in crust thickness). In a model of NH_3 emissions from slurry storage, Olesen and Sommer (1993) estimated the resistance to transport of NH_3 due to the slurry surface to be 18 s m^{-1} for a pig slurry with no crust and 119 s m^{-1} for a pig slurry with a thin crust (0.5–1 cm). It might be expected that resistance would increase with increasing crust thickness, thereby reducing the emission rate. However, the nature and integrity of the crust will also be important. We might expect that a wet crust would have a lower resistance value and be less efficient at reducing emissions, as the emitting surface is at the crust surface and not below the crust. There was some evidence of this in Experiment 3, where there was a trend for emission rates from DM2 to remain higher than those from DM3 or DM4 up to Day 70, for which period the crust on DM2 was wet but that on DM3 and DM4 was dry. However, this could equally be related to differences in crust thickness over that period (Fig. 4). Unfortunately, the wetting regime imposed in Experiment 5 did not prevent the crust from drying (possibly due to the lower impact of droplets from a watering can rose as compared with rainfall), so this effect has yet to be rigorously tested.

Factors other than crust presence or crust thickness will also influence NH_3 emissions from stored cattle slurry. These include slurry pH, temperature, wind speed, and slurry DM content (Olesen and Sommer, 1993), which will influence the proportion of TAN present as gaseous ammonia in the aqueous-ammonium/aqueous-ammonia/gaseous-ammonia equilibrium in the slurry, the replenishment rate of surface TAN by diffusion and convection, and the transport of NH_3 across the slurry surface and into the free atmosphere. Differences in, and interactions between these, and interactions between their relative influence on NH_3 emission rate and crust development could account for the differences observed in this study in normalized emission rates between experiments.

Factors Influencing Crust Development

Within these experiments, slurry DM content was the major factor influencing crust formation. The only slurries that did not form a crust during storage were those with a DM content of <1%. This concurs with the hypothesis that crust formation results from gas bubbles (carbon dioxide and methane) forming within the slurry carrying particles to the slurry surface, where, if present in sufficient quantities, they will coalesce and form a crust. Slurry DM content has been related to methane production within pig slurry stores (Martinez et al., 2003). Increasing DM content may, therefore, be having a dual effect on crusting by increasing both the number of gas bubbles arising within the slurry and the number of particles available to be carried to the surface. The nature of the DM may also be important. In Experiment 5, the slurry from the cattle fed different diets developed quite different crusts. No objective measurements were made as to the nature of the slurry DM content but, subjectively, the slurry from the grass silage–fed cattle was more viscous and contained more fibrous material than that from the corn silage–fed cattle. One important difference in the sources of these slurries was that the cattle fed the grass silage–based diet were bedded on long straw whereas those fed the corn silage–based diet were bedded on chopped straw. Although Experiment 1 indicated that bedding material was not an important influencing factor, long straw was not included as one of the treatments.

Crust thickness varied between experiments, ranging from 0 to 38 cm. Generally, if slurry DM content was sufficiently high (>1%), a measurable crust would begin to form within the first 10 to 20 d of storage. Crust thickness would then stabilize after 40 to 60 d, after which time the crust tended to become dryer and harder (subjective observations). It might be expected that temperature would be an important factor influencing crust formation as it would influence both methane production rate within the slurry (Husted, 1994) and the evaporation rate and hence drying of the forming crust at the slurry surface. However, there is no strong evidence of a temperature effect from this study. Crusts took approximately 30 d to form, for both the coldest (Experiment 1) and warmest (Experiment 3) storage conditions. One weakness of this study, however, was the lack of a consistent “control” treatment, which would have facilitated objective comparisons between different experiments. Equally, air flow rate across the slurry surface might have been expected to influence surface drying and, therefore, crust development, but this was not apparent from the results of Experiment 4. Indeed, crusts formed and dried rapidly, despite the flow rates being relatively low; Scotford and Williams (2001) reported wind speeds above a slurry storage lagoon of 0.8 to 4.0 m s^{-1}. Wind speeds above the slurry surface of a circular store could be much lower, depending on the diameter of the store and the distance between the slurry surface and the top of the store walls.

Reduction of NH_3 volatilization from livestock wastes has been shown to be feasible through the use of additives, particularly those with acidifying or adsorbent properties (McCrory and Hobbs, 2001). Addition of a labile carbon source, such as the corn starch used in this study, stimulates the production of organic acids by the indigenous anaerobic microorganisms (Subair, 1995; Hendriks and Vrielink, 1997) and may represent one of the more practical options. McCrory (2003) showed in a laboratory study that small inclusion rates of the corn starch additive (0.2% w/v) applied to the surface layer were equally effective at reducing NH_3 emissions as higher inclusion rates mixed in with the slurry. The inclusion of the labile carbon will also promote carbon dioxide and methane production within the slurry (Martinez et al., 2003) and, according to our hypothesis, crust formation. This was confirmed by the increase in crust thickness when the corn starch additive was used, with substantially more crust development with the additive containing the most labile carbon (Fig. 8). The reduction in NH_3 emissions achieved through the use of the additive in this study (Fig. 7) is due both to a lowering of the slurry pH and formation of a surface crust, although from the data in this study it is not possible to determine the proportional effect of each of these modes of action.

Natural crusting of slurry may have additional benefits. Floating covers have been shown to reduce odor emissions from slurry storage (Bicudo et al., 2004) and there is no reason to suspect that a crust would not have the same effect, increasing the resistance to transport of odorous molecules across the surface layer. Sommer et al. (2000) reported that crusting reduced methane emissions from slurry storage, suggesting that methane was being oxidized to carbon dioxide as it moved through the surface crust.

CONCLUSIONS

The most important factor influencing crust formation is slurry DM content; in this study crusts did not form on slurries with a DM content of <1%. The diet of the cattle is also important, influencing the nature of the slurry DM; large differences were observed in crust formation on slurries from cattle fed corn silage– or grass silage–based diets. Bedding types used in the free stall barn did not influence crust formation. Increasing air-flow rate over the slurry surface increased NH_3 emission rate, but did not significantly influence crust formation.

The formation of a natural crust on dairy cattle slurry stores will reduce NH_3 emissions compared with noncrusted stores by approximately 50%, although this was inconsistent between experiments. Even the formation of a thin “skin” was effective at reducing emissions. This suggests that farmers should aim to maintain a manageable crust on stores throughout the storage period, rather than regularly agitate stores to prevent crust formation as advised in the past (Grundy, 1980). Further research should be aimed at examining the physical and chemical processes of crust formation and developing objective measurements of crust parameters (thickness, integrity, wetness, porosity), which could be related to the slurry surface resistance parameter in emission models. It should also be borne in mind that reductions in NH_3 emission at the manure storage stage will result in increased manure TAN content and potentially larger losses following land-spreading unless suitable application or incorporation methods are used to minimize losses from that stage also.

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